

Surface freezing in mixtures of molten alkanes and alcohols

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Received 26 September 1996

Abstract

Surface freezing is studied in molten binary mixtures of alkanes and alcohols of different lengths using X-ray surface scattering and surface tension measurements. A crystalline monolayer (for alkanes) or bilayer (for alcohols) is formed at the surface a few degrees above the bulk freezing temperatures. The behaviour is found to be dominated by the length difference of the two components, Δn . For small Δn the surface properties and structure vary continuously with concentration between those of the pure components. For large Δn , however, the variation is discontinuous, exhibiting surface segregation. Several new phenomena, not observed in the pure components, are also found: a new surface crystalline structure in alkanes, a suppression of surface freezing for some compositions in both materials, and the inducement of surface freezing in alcohols which do not show the effect when pure. A Flory–Huggins theory based on competition between entropic mixing and a repulsive interaction due to chain length mismatch accounts well for the observed phenomena in alkanes, but requires modifications when applied to alcohols, probably due to the more complex additional headgroup interactions. © 1997 Elsevier Science B.V.

Keywords: Surface freezing; Alkane mixtures; Alcohol mixtures

1. Introduction

Molecules residing at the free surface of solids are less confined, and consequently have a higher entropy at a given temperature, than molecules in the bulk [1,2]. Thermodynamics predicts, therefore, that, in general, the surface of a solid will melt at a lower temperature than the bulk. This effect, known as surface melting, has been observed in numerous systems ranging from ice [3], through

metals [2] to molecular crystals [4]. Very recently we [5–7], and others [8], have demonstrated the existence of the opposite, much more rare, surface freezing phenomenon in pure monodisperse liquid normal-alkanes [5–7] [$\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3$, abbreviated C_n] and alcohols [9] [$\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}$, abbreviated as C_nOH]. Here a crystalline monolayer is formed on the surface of the melt at a temperature T_s of up to a few degrees above the bulk freezing point T_f , where the bulk is still liquid. While this behaviour clearly results from a delicate balance between the bulk and surface free energies, the molecular-level basic science underlying this

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behaviour is still unclear. To gain a better understanding, we have studied the surface behaviour of liquid binary mixtures of normal-alkanes and normal-alcohols of different chain lengths, where the bulk free energies can be tuned conveniently by varying the molecular lengths and the compositions. The results of this study are reported here. As we show below, mixing allows access to regions in the phase space where new phenomena, not occurring in the pure components, can be observed and studied. Furthermore, a comparison of the behaviour of alkane mixtures with that of alcohol mixtures results in a better understanding of both, of the basic theory underlying the behaviour, and of the deviations from ideality in some mixtures. In addition, in real world applications such as in lubricants, paints, solvents, oil products, etc. these molecules occur almost always as mixtures rather than pure, single component materials. The results reported here are, therefore, of importance not only to basic science but also to applied science and industrial applications.

Since the surface behaviour of a mixture is intimately related to that of its pure constituents, we now summarize the results obtained for surface freezing in pure alkanes and alcohols. In both cases a crystalline layer is formed at the surface at a temperature $T_s > T_f$, where T_f denotes the bulk freezing temperature. However, while for alkanes a single monolayer is formed, for alcohols a single bilayer is obtained, with the two OH headgroups residing at the centre of the bilayer. For all materials studied the formation of the surface layer is a first-order transition to within a few mK. Once formed, the structure of the layer remains unchanged by further cooling to the bulk freezing at T_f . The temperature range of the existence, $\Delta T = T_s - T_f$, of this surface crystalline phase has a non-monotonic dependence on the molecular length n . For alkanes, the surface freezing effect occurs for $16 \leq n \leq 52$, and ΔT has a maximum of about 3°C for $n \sim 20$. The monolayer has in this case a long-range positional and orientational order with a crystalline coherence length of at least a few thousand Å. The monolayer is in the rotator phase [10] for lengths $n < 44$, with hexagonally packed molecules, which are oriented normal to the surface for $n < 30$, and tilted towards their

nearest neighbours for $n \geq 30$. For $n \geq 44$ the surface phase is a non-rotator crystal with molecules tilted towards their next-nearest neighbours.

In pure alcohols, the surface freezing effect occurs only for even carbon numbers in the range $16 \leq n < 30$, with a maximum temperature range of $\Delta T \approx 1.5^\circ\text{C}$ at $n \sim 22$. The packing in the bilayer is again hexagonal with molecules vertical for $n < 24$ and tilted in the next-nearest neighbour direction for $n \geq 24$. The hexagonal lattices in the upper and lower layers of the bilayer are shifted one relative to the other in the next-nearest neighbour direction by $1/\sqrt{3}$ of the lattice spacing. The reduced molecular length range for which surface freezing occurs in alcohols as compared to alkanes reflects a lower tendency for surface freezing in alcohols. Both the non-tilted/tilted (in alcohols and alkanes) and surface rotator/non-rotator (in alkanes only) phase transitions clearly appear in the variation of the measured layer thickness, surface roughness, ΔT , etc. with n . Further details are given in Refs. [5–7] for pure alkanes and in Refs. [9,11] for pure alcohols.

In the study reported here, a similar first-order surface freezing transition is observed in binary mixtures of molten alkanes and alcohols, resulting in the formation of a crystalline monolayer for alkane mixtures and a bilayer for alcohol mixtures. However, since the interactions among the molecules and their affinity for the surface differ with chain length, both the temperature range of existence of the surface-frozen phase and the surface composition vary with the chain length difference Δn and bulk composition. By varying the concentration in the bulk liquid it is possible to fine-tune the free energy balance and obtain for a particular range a complete exclusion of one of the components from the surface or even a complete suppression of the surface freezing effect. For mixtures with small Δn , the crystalline surface layer is a homogenous mixture of the two components. For large Δn , only one component of the bulk binary mixture appears in the surface crystalline layer. Using surface X-ray techniques and surface tensiometry, we have studied extensively two families of alkane mixtures, $C_{20}-C_{20+\Delta n}$ and $C_{36-\Delta n}-C_{36}$, where Δn ranges from 2 to 18, and one family of

alcohol mixtures, $C_{18}OH-C_{18+\Delta n}OH$, where Δn ranges from -4 to 10 . Although the basic trends observed for the two materials are similar, the details of the alcohol mixture phase behaviour still differ significantly from those of the alkane mixtures, indicating that alcohol mixtures have additional interactions which result in deviations from ideal mixture behaviour. These results are discussed below in detail.

2. Experimental

The samples were prepared by thoroughly stirring a preweighed, molten mixture of commercial alkanes or alcohols of purity $\geq 99\%$. The molten mixture was poured onto a clean silicon wafer mounted in a sealable cell, the temperature of which was regulated to < 5 mK. The surface structure of the liquid mixture was studied as a function of temperature by X-ray reflectivity (XR) and X-ray grazing incidence diffraction (GID), using the Harvard/BNL liquid spectrometer at beamline X22B of the National Synchrotron Light Source. XR yields information on the electron density profile normal to the surface [12], such as the thickness, density and roughness of a surface layer. GID measurements provide information on the structure of a layer within the surface plane [13]. The magnitude and direction of the molecular tilt is obtained from measurements of the Bragg rods (BR), i.e. the surface-normal variation of the scattered intensity at the position of each in-plane GID peak.

The thermodynamic properties of the surface in the liquid and crystalline phases were studied by surface tension (ST) measurements, using the Wilhelmy plate method [7,14]. These measurements provide information on the excess free energy of the molecules at the surface over those in the bulk. The formation of the layer at T_s results in a sharp change from a negative to a positive slope in the surface tension $\gamma(T)$. The resultant difference $\Delta(d\gamma/dT)$ of the slopes below and above T_s equals the surface entropy change upon surface freezing. Further details on the experimental techniques and computer fitting methods employed to

extract the various quantities discussed below from the measurements are given elsewhere [6].

3. Results and discussion

Figs. 1 and 2 show XR measured off the free surface of a 1:1 mixture of C_{20} – C_{24} alkanes and two different mixtures of $C_{18}OH$ – $C_{22}OH$ alcohols, respectively, as well as for the corresponding monodisperse components. At $T > T_s$, no surface layer is present, and a monotonic fall-off with q_z , typical of an isotropic liquid surface [15,16], is observed for all samples, similar to that denoted liquid in Fig. 1. In the temperature range $T_f \leq T \leq T_s$, the XR curves for all samples exhibit pronounced modulations, indicating the existence of a surface layer with an electron density different from that of the bulk. The different modulation periods reflect different average surface layer thicknesses D . The periods of the mixtures are intermediate between those of the pure components, indicating an effective layer thickness D which is also intermediate between those of the pure components. More spectacular is the roughly twice smaller modulation period of the alcohols in Fig. 2 as compared to the alkanes in Fig. 1. This indicates a D twice as large as that of alkanes of comparable lengths, i.e. a bilayer structure, both for the pure alcohols and their mixtures.

For quantitative analysis, models were constructed for the density profile of the layer and fitted to the XR data, using the widely used matrix and Born approximation methods [6,12]. The model for the alkanes assumes a layered interface consisting of a slab of higher electron density, representing the ordered $(CH_2)_{n-2}$ chains, and a lower density depletion zone at the bilayer–liquid interface, corresponding to the less dense CH_3 groups. This is the same model used to fit the crystalline monolayers of the monodisperse alkanes [5,6]. The excellent fit obtained with this model, shown as solid lines in Fig. 1, yields the density profiles shown in the inset for the pure components (a,c) the mixture (b) and the liquid surface phase (d). A 15% increase in the density of the surface layer over that of the liquid bulk is found for all mixtures, as for the pure components

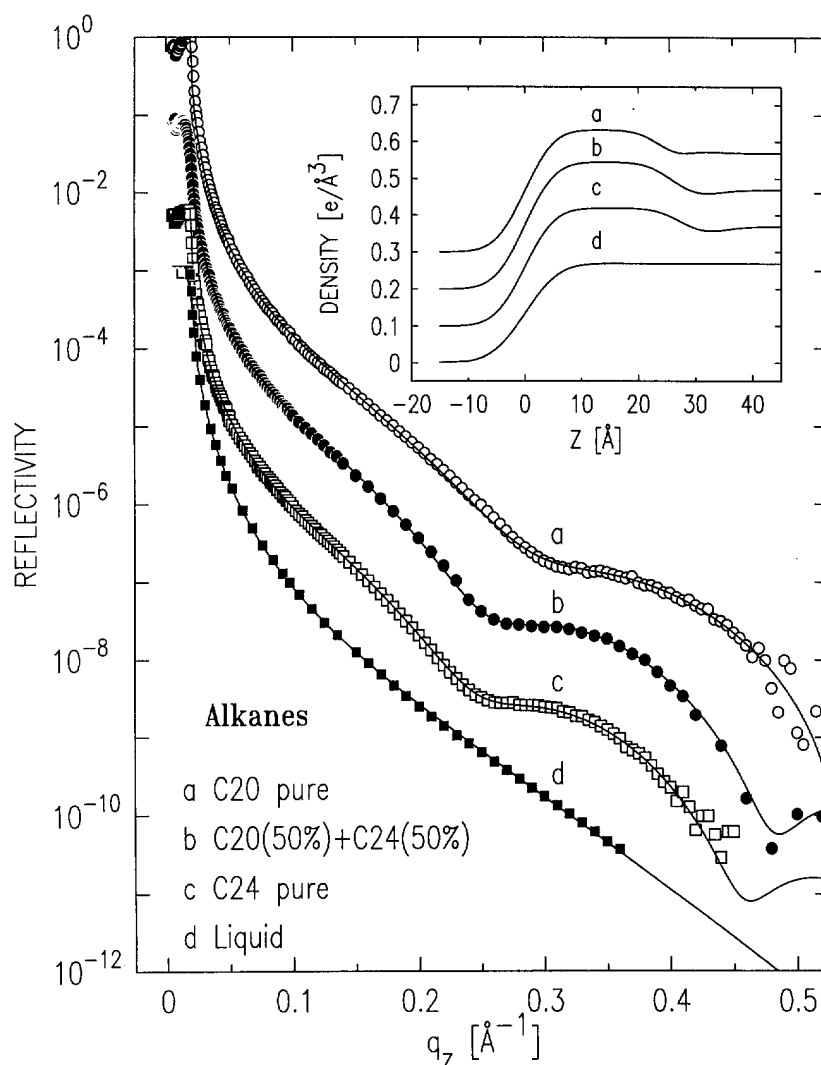


Fig. 1. X-ray reflectivities from the free surface of molten n-alkanes C_{20} and C_{24} in their surface crystalline phase and their 1:1 mixtures in both the surface crystalline and the higher temperature liquid surface phases. The solid lines are fits of model density profiles shown in the insets. The reflectivities and the density profiles are shifted for clarity.

[5,6], and we obtain for the mixture an intermediate D between those of the two pure constituents. This indicates that structurally the mixture behaves similarly to a monodisperse alkane of intermediate chain length in this case. This is similar to what is observed in binary mixtures of close homologues in several liquid crystal families [17].

The model used to fit the alcohol mixture data in Fig. 2 is slightly more complex, having to

account for the internal structure of the bilayer. An attempt to use a single slab of a constant density to represent the average density of the bilayer resulted in a very poor fit. To obtain the excellent fits shown by the solid lines in Fig. 2 it was necessary to add a thin, high-density layer at the centre of the bilayer and a lower density depletion layer at each of its boundaries, as shown in the inset to Fig. 2 (the upper depletion layer, at

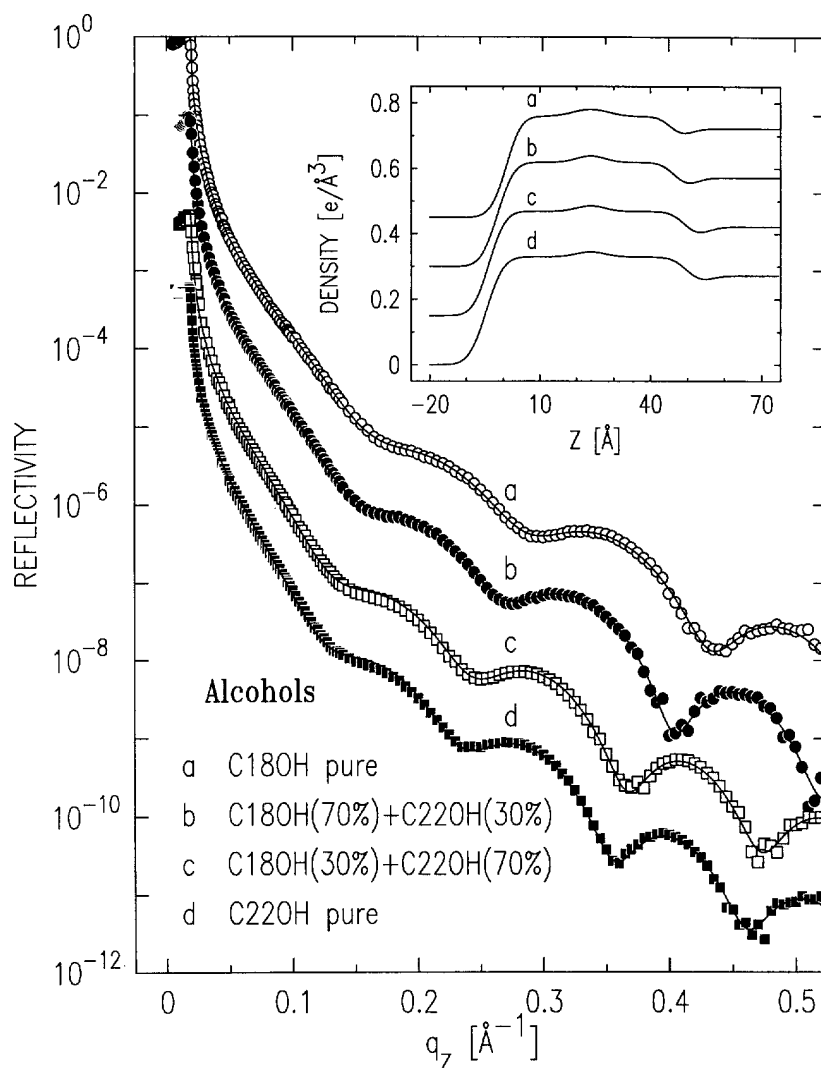


Fig. 2. Same as Fig. 1, but for two different mixtures of molten $C_{18}OH$ and $C_{22}OH$ alcohols and the pure components, in their surface crystalline phases. Note the increased density at the center of the bilayer in the density profiles in the inset, which is due to the layer of OH groups.

the free surface, is masked by the strongly decreasing profile in this region). This model indicates that the molecules in the upper and lower layers are positioned head to head, with the central high-density slab representing the denser layer of OH groups and the two low density boundary layers the terminal CH_3 groups. As is the case for alkanes, this structure is identical to that of the surface layer of the pure constituents [9,11]. Except for

the bilayer/monolayer difference the XR fit of the alcohol mixture in Fig. 2 shows the same properties as the alkane mixture in Fig. 1: a surface layer density $\sim 15\%$ higher than that of the bulk liquid and a D value intermediate between those of the two pure components.

A careful examination of the chain length dependence of the mixtures' measured surface layer structure reveals that the quantity which dominates

the behaviour in both alkanes and alcohols is the relative chain length difference of the two components, $\Delta n/\bar{n}$, where \bar{n} is the average of the two chain lengths. The specific choices of n were found to play only a minor role in determining the behaviour. We find dramatically different behavioural trends for small- and large- $\Delta n/\bar{n}$ mixtures, with similar characteristics for both materials and many combinations of chain length. As an example, we show in Fig. 3(a–d) the XR-measured thickness vs. composition of the surface layers for four typical mixtures: $C_{30} + C_{36}$ and $C_{18}OH + C_{22}OH$, representing the small- $\Delta n/\bar{n}$ mixtures, and $C_{26} + C_{36}$ and $C_{18}OH + C_{28}OH$, representing the large $\Delta n/\bar{n}$ mixtures. Note that for each Δn the trends in the figures are the same for the alcohols and alkanes.

For the small- Δn mixtures of both alkanes and alcohols, shown in Fig. 3(a,d), the average D varies continuously and monotonically with ϕ_{long} (the volume fraction of the long component in the bulk liquid), between those of pure short (D_{short}) and pure long (D_{long}) components. The continuous variation of D implies a continuous change in the composition of the surface crystalline layer. The solid curves are the values of D calculated using the expression $D = \phi^{\text{cs}} D_{\text{short}} + (1 - \phi^{\text{cs}}) D_{\text{long}}$, where ϕ^{cs} is the concentration of the short component in the surface crystalline layer, as derived from the theory discussed below.

The large- Δn mixtures in Fig. 3(b,d) exhibit, by contrast, a dramatically different behaviour. The thickness D varies *discontinuously* with ϕ_{long} . For the alkane mixture, it takes on three discrete values, shown as solid lines in Fig. 3(b). For $\phi_{\text{long}} < 20\%$, and $\phi_{\text{long}} > 60\%$, the measured D are those of pure short (D_{short}) and long (D_{long}) components, respectively, rather than an intermediate value, as found for small- Δn mixtures. In both cases the surface crystalline layer appears to consist, therefore, of a single component: either the short or the long one. For a range of ϕ_{long} between 20 and 30% (the shaded region in Fig. 3(b)) the surface freezing effect disappears completely. Finally, for $30\% < \phi_{\text{long}} < 60\%$, a new surface phase appears via a first-order transition [18,19]. In this region D is even slightly larger than D_{long} . A similar division into four regions, with identical

temperature boundaries, is observed in the surface tension measurements. The large- Δn alcohol mixtures, Fig. 3(d), exhibit the same behaviour as alkanes: a macroscopic surface phase separation occurs, where for $\phi_{\text{long}} > 75\%$ the surface phase consists of the pure long component only and for $\phi_{\text{long}} < 15\%$ it consists of the short component only. These two concentration regions are again separated by a concentration range, $15\% < \phi_{\text{long}} < 75\%$, where the formation of the surface layer is pre-empted by bulk freezing and no surface bilayer is formed. Note also that a third phase, observed in the alkane mixtures for $30\% < \phi_{\text{long}} < 60\%$, is not detected in our measurements in alcohol mixtures.

The GID measurements for all small- Δn mixtures investigated by us show in-plane structures identical to those of the pure materials [5,6,9,11] with the provision that if one component, when pure, has a tilted surface phase the mixture will also exhibit a tilted surface phase. For the phase-separated, large- Δn alkane mixture shown in Fig. 3(b), the GID measurements show, again, the same in-plane order in the surface bilayer as that in the corresponding monodisperse phase, excluding for the moment the third phase mentioned above. For example, for the ordinary, $\phi_{\text{long}} > 60\%$ surface crystalline phase in the alkane mixture, where the pure long molecule resides at the surface, we find two GID peaks, one at $q_z = 0$ and another at $q_z \approx 0.38 \text{ \AA}^{-1}$, with a resolution-limited in-plane peak at $q_{\parallel} = 1.48 \text{ \AA}^{-1}$ for both (q_{\parallel} and q_z denote here the wavevector transfer parallel and perpendicular to the surface, respectively). As detailed in Refs. [5,6] these are consistent with molecules tilted towards their nearest-neighbours (NN) by 18° , exactly as found for pure monodisperse C_{36} . The molecules' centres of mass are packed hexagonally when viewed normal to the layers, however the packing is distorted-hexagonal when viewed along the molecular axis. For the new surface phase, observed in the alkane mixture in the range $30\% < \phi_{\text{long}} < 60\%$, the position q_{\parallel} of the in-plane peak remains the same, but no peak is observed in the Bragg rod at $q_z = 0$. Instead, a peak now appears at $q_z \approx 0.17 \text{ \AA}^{-1}$. This is consistent with a tilt towards next-nearest neighbours (NNN), with the tilt angle reduced from 18° to 13.5° . This, in

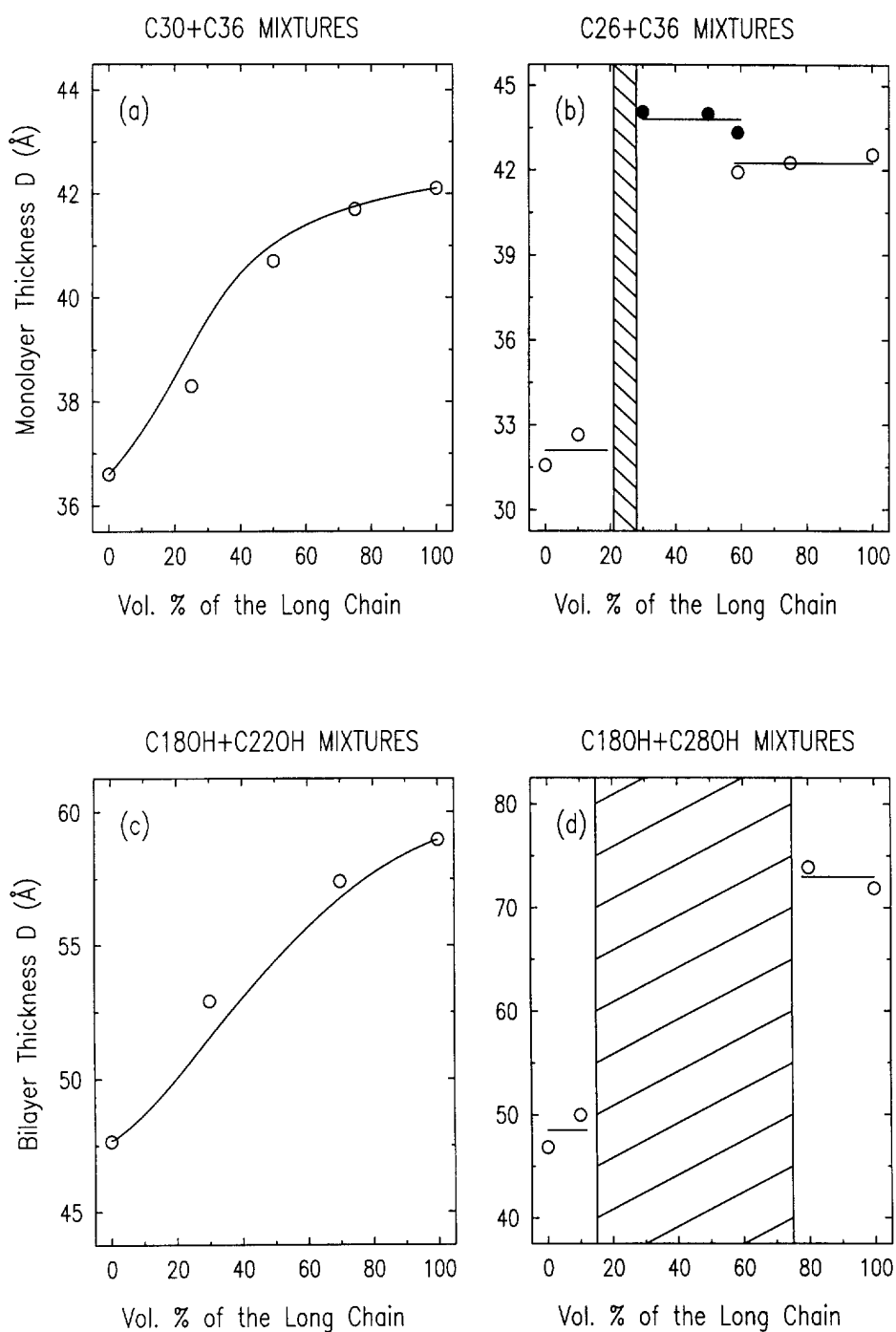


Fig. 3. The crystalline layer thickness of (a) the alkane mixture C_{30} – C_{36} representing the small- Δn behaviour, (b) the alkane mixture C_{26} – C_{36} representing the large- Δn behaviour, (c) the small- Δn alcohol mixture $C_{18}OH$ – $C_{22}OH$ and (d) the large- Δn alcohol mixture $C_{18}OH$ – $C_{28}OH$. The solid circles in (b) denote the new surface phase. Surface freezing is absent in the shaded regions. Note the continuous behaviour for the small- Δn mixtures and the discontinuous behaviour for the large- Δn mixtures.

turn, should increase the layer thickness D , as is indeed observed in the values of D derived from the reflectivity measurements. This behaviour is consistent with a thermally driven transition between a surface rotator phase with NN tilt and a surface non-rotator crystal phase with NNN tilt [6]. Note, however, that packing with NNN tilt also entails a second peak, though of a much lower intensity, along the Bragg rod at $q_{z1} = 2 \times q_{z2}$. This was not observed in the measurements. While this may be due to the expected low intensity, in the absence of this peak other structural models cannot be ruled out completely.

The slope difference $\Delta(d\gamma/dT)$ of the surface tension $\gamma(T)$ below and above T_s , shown in Figs. 4(a) and 5(a), is equal to the entropy loss ΔS of the surface layer upon freezing [6,7]. In monodisperse alkanes and alcohols $\Delta(d\gamma/dT)$

increases linearly with carbon number. In mixtures, they are displayed in Fig. 4(a) as a function of the bulk composition for samples of various Δn . In this figure we see that for alkane mixtures of $\Delta n < 8$, $\Delta(d\gamma/dT)$ changes continuously and monotonically between the values of the two pure components, as found for D in Fig. 3, implying, again, a continuous change in the composition of the surface crystalline layer. For alkane mixtures of $\Delta n \geq 8$, we see that $\Delta(d\gamma/dT)$ takes on the discrete values of the pure components, indicating that only one component is present in the surface crystalline phase. These single component surface phase regions are separated from one another by a region where the surface freezing is suppressed. This could result from frustration due to the competition between closely matched surface segregation affinities of the two species. The alco-

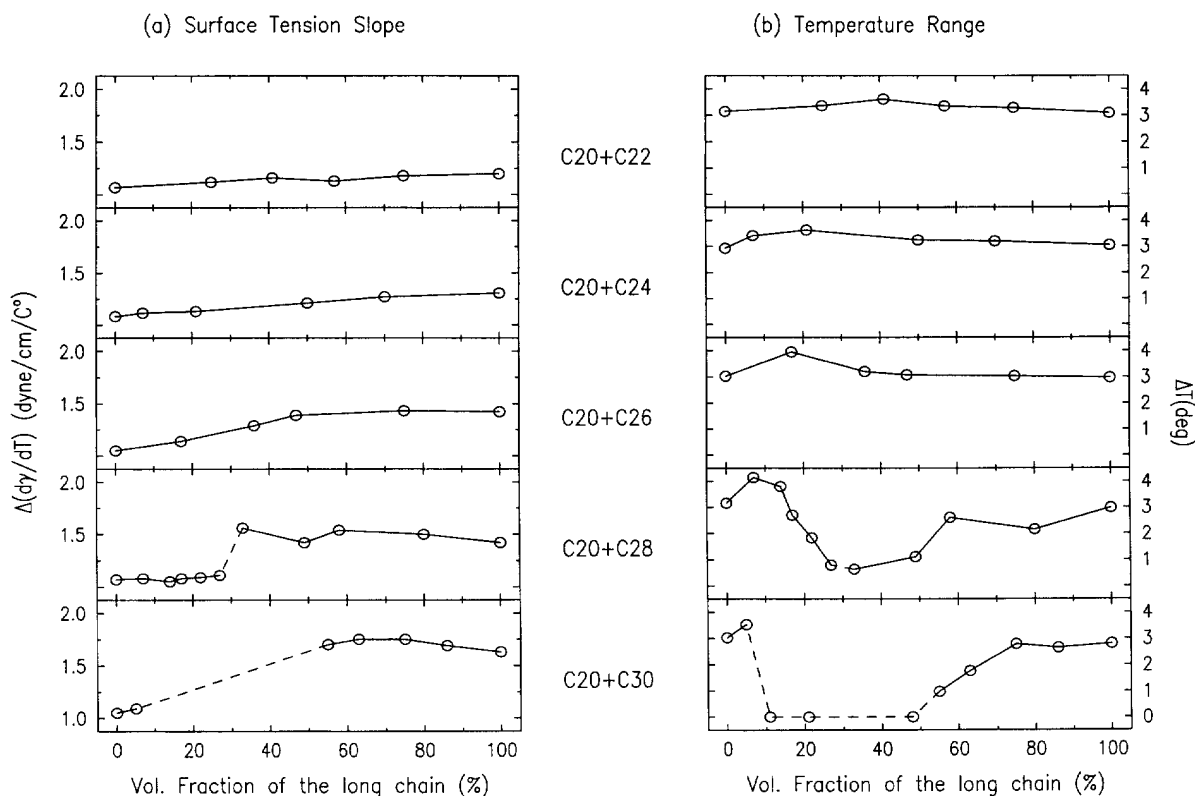


Fig. 4. $C_{20} - C_{20 + \Delta n}$ mixtures, with Δn varying between 2 and 10. (a) The slope difference of the surface tension, $\Delta(d\gamma/dT) = \Delta S$, as a function of the liquid bulk composition. (b) The temperature range of existence, ΔT , of the crystalline surface layer. The lines connecting the points for each mixture are guides to the eye, and the dashed line marks the regions where surface freezing is suppressed.

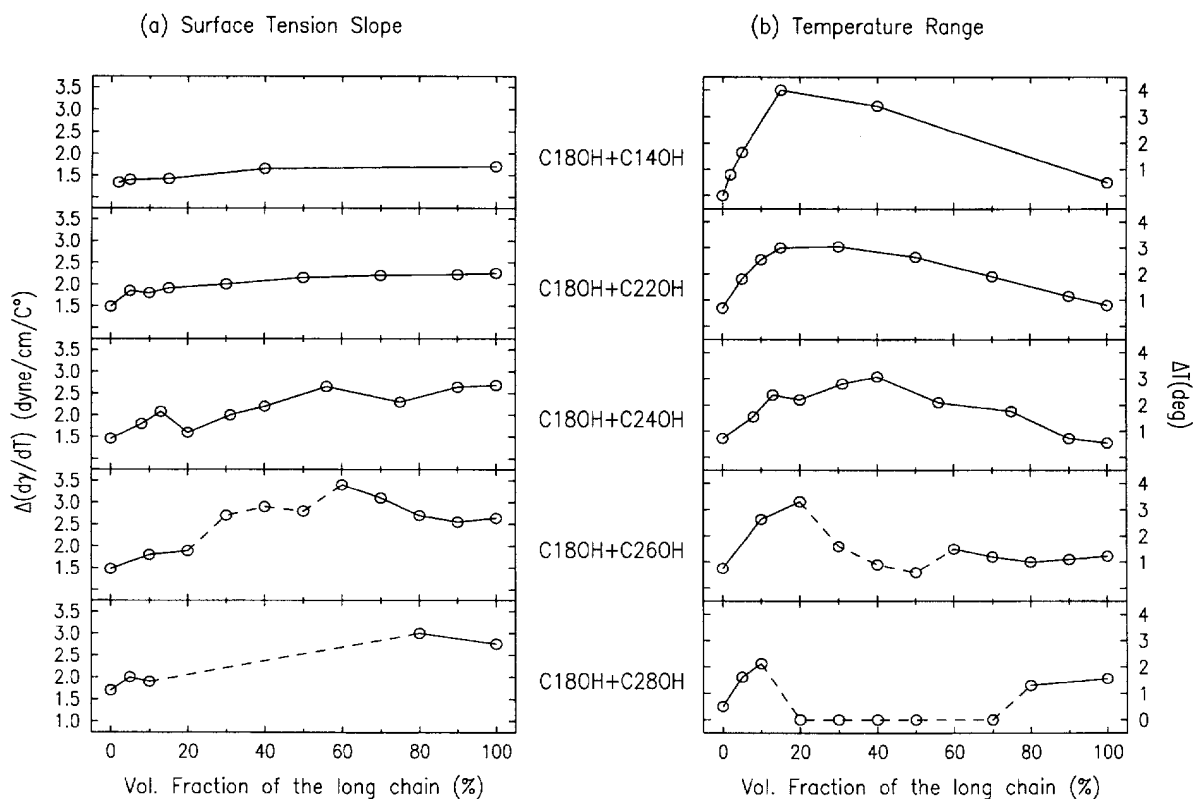


Fig. 5. Same as Fig. 4 for the alcohol mixtures indicated. Note the non-constant ΔT and ΔS , peaking at a finite concentration, for small Δn values. This deviation from the behaviour of the corresponding alkanes in Fig. 4 is discussed in the text, as is the metastable region marked by the dashed lines.

hol mixtures in Fig. 5 show a similar behaviour, and, again, $\Delta n \approx 8$ seems to be the limiting value separating large- Δn and small- Δn behaviours in these figures. Although a clear region of lower or higher $\Delta(d\gamma/dT)$ and/or ΔT , indicative of a new phase, was not detected for alcohol mixtures, the range $20\% < \phi_{\text{long}} < 60\%$ for C₁₈OH + C₂₆OH mixtures shows some peculiarities in both of these quantities. These may indicate a different phase, or, more likely, a metastable, non-equilibrium monolayer, which is nucleated only by the Wilhelmy plate. Indeed, a recent first attempt to observe the appearance of a monolayer in this composition range by X-rays failed to show the effect. Further measurements on this issue are clearly called for.

The temperature range of existence of the surface crystalline phase, ΔT , is shown in Figs. 4(b) and

5(b) as a function of the bulk composition for mixtures of alkanes and alcohols of progressively larger Δn . Similar to the observations for D in Fig. 3, and $\Delta(d\gamma/dT)$ in Figs. 4(a) and 5(a), a dramatically different behaviour is observed for small and large Δn . For the alkanes, Fig. 4(b), when $\Delta n < 8$, ΔT varies smoothly and very slowly with n . For $\Delta n \geq 8$, however, ΔT changes abruptly with bulk composition, and a range exists where surface freezing is suppressed completely (i.e. $\Delta T = 0$). This range increases with increasing Δn . This behaviour results from the fact that the ϕ dependencies of the two transition temperatures T_s and T_f are very different for these Δn 's. A similar trend of a continuous ΔT for small- Δn and a discrete one for large- Δn is observed for the alcohol mixtures, Fig. 5(b). However, the shape of $\Delta T(\phi)$ deviates considerably from the constant ΔT

observed in the corresponding alkanes. ΔT in alcohol mixtures peaks at some intermediate concentration, which moves consistently with increasing Δn towards higher concentrations. More significantly, it reaches ΔT values up to four-fold higher than the $\Delta T \leq 1\text{--}1.5^\circ\text{C}$ of the pure alcohols. The large- Δn behaviour is also somewhat different: while phase separation indeed occurs, ΔT increases considerably in the low ϕ_{long} region, as can be seen for the $\text{C}_{18}\text{OH} + \text{C}_{26}\text{OH}$ and $\text{C}_{18}\text{OH} + \text{C}_{28}\text{OH}$ mixtures. Nevertheless, the X-ray measurements confirm that for the $\text{C}_{18}\text{OH} + \text{C}_{28}\text{OH}$ mixture throughout the range from $\phi_{\text{long}} = 0\%$ to $\phi_{\text{long}} \approx 10\%$ where the effect vanishes, the surface bilayer remains a pure C_{18}OH layer.

The phase behaviour of the alkane mixtures discussed above, and, in particular, the strong Δn dependence, can be accounted for extremely well by a Flory–Huggins-type theory of binary mixtures [18]. The system energetics in this theory are basically determined by two competing interactions: the entropic mixing and the chain length mismatch repulsion [20]. The first of these drives a uniform mixing of the two components. The second tries to minimize the contact between chains of different lengths, i.e. drives for phase separation of the two components. The equilibrium state is determined by the balance of the two for the chain lengths n present in the mixture. Computationally, the free energy of each component, both in the bulk and the surface, is written in terms of the properties of the pure components and the composition of the bulk liquid mixture, which are used as the free variables. The chemical potentials derived from these free energies for the liquid and the solid are then equated at the coexistence temperature, either T_s or T_f , for the surface and the bulk, respectively. Using the measured values of these temperatures we obtain the composition in the crystalline phase at coexistence ϕ^{cs} and the value of the dimensionless repulsion parameter χ . The repulsive interaction due to chain length mismatch is found to be $\chi \sim (\Delta n/\bar{n})^2$. This is in excellent agreement with the dominant dependence on Δn observed experimentally and the symmetry required of the system. This simple thermodynamic model was found to account well quantitatively for the overall phase behaviour,

including the transition temperatures and the surface and bulk compositions. As an example, the prediction of this theory for D is given as the solid line in Fig. 3(a) and it can be seen to be in very good agreement with the measurements. The same is true for the measured $\Delta(\text{d}\gamma/\text{d}T)$ for the various concentrations [18]. The theory accounts, in particular, for the fact that for $(\Delta n/\bar{n}) \approx 8/32 \approx 0.25$ the surface crystalline layer changes from mixed, continuous behaviour to segregated, discontinuous behaviour. Further details can be found in Refs. [18,19].

In contrast to the excellent agreement obtained for alkane mixtures with the simple Flory–Huggins theory [18], the alcohol mixtures show significant deviations from this simple picture [19] which is well known for the bulk behaviour of such associating liquids. While the same theoretical approach is basically still valid, the peculiar shape of ΔT , which shows a maximum at $\phi \neq 0,1$, requires a modification of the free energy to allow a good fit to the measured coexistence temperatures. Preliminary results show that these modifications can take the form of either a more complicated interaction term than the simple Flory–Huggins one, or by assuming the existence of some restrictions on the allowed packing in the bulk, which will reduce the entropic contribution to the free energy by a factor of approximately 2. At this stage no preference can be given to one possibility over the other. We note, however, that both lead to a good agreement of the theory with the experiment, as demonstrated by the theoretical fit shown as a solid line in Fig. 3(c). This point is currently under further theoretical and experimental investigation [19].

Finally, we note that mixing allows us to tune the free energies such that regions in phase space can be reached which are inaccessible with the pure constituents of the mixture. Whereas no surface freezing is observed for pure C_{12}OH , a surface-frozen bilayer can be induced in this material by mixing in small quantities of longer-chain alcohols. As an example, we show in Fig. 6 the XR data obtained for (90%) $\text{C}_{12}\text{OH} +$ (10%) C_{18}OH . The modulations clearly show the existence of a surface crystalline bilayer, and the fit, shown as a solid line, proves the surface crystalline

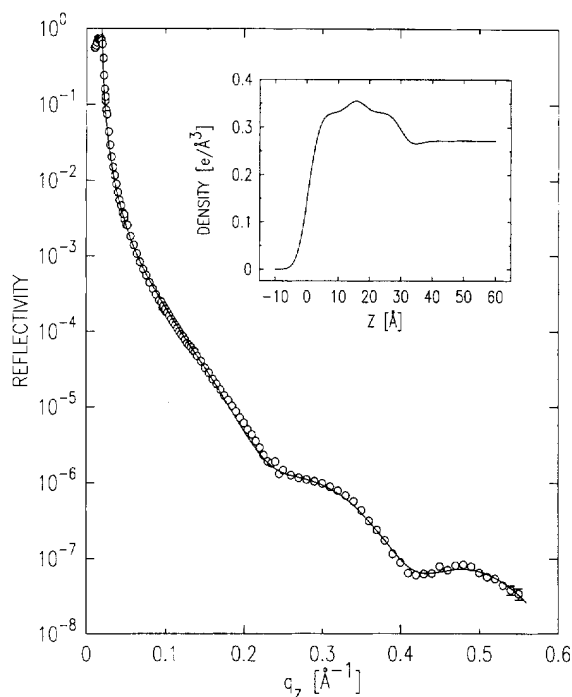


Fig. 6. The measured X-ray reflectivity (\circ) of a 90% $C_{12}OH$ –10% $C_{18}OH$ alcohol mixture at a temperature of $\sim 1^\circ C$ above the bulk freezing temperature. The modulations indicate the existence of a surface layer. The model fit (—) and the resultant density profile given in the inset clearly show the surface-frozen solid layer to be a $C_{12}OH$ bilayer, even though the pure alcohol $C_{12}OH$ does not show surface freezing.

layer to be a $C_{12}OH$ bilayer, monodisperse to within the measurement error. The corresponding density profile is shown in the inset. The temperature range of existence is found to be $\Delta T \approx 1.5^\circ$. We remind the reader that the shortest pure alcohol showing surface freezing is $n = 16$ [9,11], and even that with only $\Delta T \approx 0.2^\circ$. Obviously, the mixing reduces T_f to a level low enough to prevent the pre-empting of the surface freezing effect by the bulk freezing.

The work presented here is, to the best of our knowledge, the first experimental molecular-resolution study of the phase diagram of the free surface of a liquid binary mixture. It reveals several rare or unique phenomena such as the surface freezing effect itself, new surface phases and surface freezing for molecules not showing this effect when pure. Δn was found to tune the system between

two dramatically different behavioural patterns, a continuous one for small Δn and a discrete one for large Δn . The study also demonstrates that an interesting level of complication is introduced by using non-symmetric molecules such as alcohols. The phase behaviour of alcohol mixtures is found to deviate from the ideal Flory–Huggins theory which accounts well for the mixtures of the symmetric alkane molecules. Clearly, further measurements are required to map out the phase diagram of these interesting binary mixtures and to understand the relations between the phase behaviour of the quasi-2D surface and the 3D bulk.

Acknowledgment

This work was supported, in part, by The Israel Science Foundation, administered by The Israel Academy of Sciences and Humanities, Jerusalem, and the Exxon Education Foundation. BNL is supported by the Division of Materials Research, DOE, under contract DE-AC02-76CH00016.

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